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On the nature of the coefficient of friction of diamond-like carbon films deposited on rubber

D. Martinez-Martinez,^{a)} J. P. van der Pal, M. Schenkel, K. P. Shaha, Y. T. Pei,^{a)} and J. Th. M. De Hosson

Department of Applied Physics, Materials innovation institute M2i, University of Groningen, Nijenborgh 4, Groningen, 9747 AG, The Netherlands

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In this paper, the nature of the coefficient of friction (CoF) of diamond-like carbon (DLC)-protected rubbers is studied. The relative importance of the viscoelastic and adhesive contributions to the overall friction is evaluated experimentally by modifying the contact load and the adhesive strength between the surface and the counterpart. The results indicate that the increase of CoF during the tribotests under non-lubricated conditions is caused by the increase of the adhesive contribution to friction motivated by the growth of the contact area during the test. In the case of oil lubricating condition, the adhesive force is minimized and the CoF is observed to decrease during the tribotest. This is caused by the reduction of the viscoelastic contribution due to the variation of the shape of the contact area. The role of the microstructure of the DLC film on the efficiency of the oil lubrication is also discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4723830>]

I. INTRODUCTION

Diamond-like carbon (DLC) films are attractive solutions as protective coatings for many applications, due to the combination of relatively high hardness, chemical inertness, low friction, and low wear rate.^{1,2} Their chemical composition, which is mainly composed of C and H, suggests a good compatibility with rubber materials. Rubber seals are incorporated in ball bearings widely used in many technical fields, like aerospace and automotive industries,³ in order to prevent the leakage of lubricant and the entrance of dirt. However, under operation dynamic rubber seals suffer from severe wear and cause high friction, leading to an ultimate failure of the bearings. Therefore, a protective coating with optimal tribological performance is of interest regarding energy saving and environmental protection.

The deposition of DLC films by plasma enhanced chemical vapor deposition (PECVD) has demonstrated to be a good choice for the protection of flexible substrates.^{4–11} In previous papers, we reported the deposition of self-segmented DLC films, which improves film flexibility without reduction of tribological performance.^{8–11} These films showed an excellent adhesion to the substrate, and the protected rubbers demonstrated negligible wear and much lower CoF than the corresponding unprotected specimens.¹⁰ Thus, no debris formation or adhesive failure was detected in the films during the tribotests. In addition, the CoF could be controlled by a proper tailoring of the film microstructure by a proper selection of the temperature differences during film growth (ΔT).^{8,9}

In all cases, the friction coefficient follows a similar trend when the number of cycles of the tribotest is increased (see Figure 2 as an example): the CoF progressively grows until a

steady state is finally reached. The number of laps needed to achieve this steady state depends on the viscoelastic properties of the rubber and the parameters of the tribotest, such as load, sliding velocity, and frequency.^{10,12} The increase of CoF is parallel to a progressive increase of the contact depth of the ball on the DLC coated rubber, indicating an influence of the viscoelastic properties of the rubber.¹⁰

Two friction components can account for the increase of CoF during a tribotest (see Figure 1). On the one hand, the adhesive component is related to the adhesive strength between the surfaces in contact. On the other hand, the viscoelastic component has its origin in the difference between the energy consumed on the front part of the ball for deforming the rubber (labeled as E_{press} in Figure 1) and the energy recovered on the back part of the ball due to the pushing by the deformed rubber (labeled as E_{push} in Figure 1). This hysteresis contribution is zero in the case of pure elastic materials due to its immediate recovery.

In previous papers,^{12,13} the evolution of the viscoelastic contribution to friction during consecutive cycles was simulated. The steady state is reached when the deformation at a point on the wear track in a previous pass is recovered in the next lap. Before reaching this state, the deformation of the rubber at one point during one pass is not completely recovered during the following lap, and therefore the overall depth increases. During this period, the viscoelastic contribution to friction decreases progressively with the number of cycles. This is a consequence of shape variation of the contact area between the counterpart and the sample, which leads to a reduction of the torque opposing to the movement. Thus, the shape of the front part of the contact area evolves from a circular shape to an elongated one, which was confirmed experimentally by using ion-etched rubbers.^{13,14} Nevertheless, the size of the contact area was observed to grow during the test. Both results indicate that the adhesive contribution to CoF should be the origin of the observed frictional behavior,

^{a)}Authors to whom correspondence should be addressed. Electronic mail: d.martinez.martinez@rug.nl and y.pei@rug.nl.

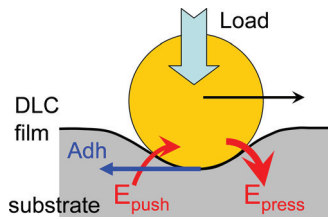


FIG. 1. Scheme of the contributions to friction between a DLC-protected rubber and the sphere counterpart during a ball-on-disk tribotest.

although no experimental validation has been provided yet. Therefore, the aim of this work is to give an experimental validation to these theoretical predictions, and to confirm the nature of the frictional behavior of DLC-protected rubbers.

II. EXPERIMENTAL DETAILS

DLC thin films were deposited on alkyl acrylate copolymer (ACM) rubbers by means of PECVD in a Teer UDP/400 close field unbalanced magnetron sputtering rig, with all the magnetrons powered off. A pulsed DC (p-DC) power unit (5 kW Pinnacle Plus, Advanced Energy) was used as substrate bias source, operating at 250 kHz with a pulse-off-time of 500 ns and voltages between 300 and 600 V. Before deposition, the rubber substrates were cleaned by two subsequent wash procedures using a detergent solution and boiling water, in order to improve the film adhesion by removal of the dirt and the wax present on the rubber surfaces, respectively.^{8,15}

The deposition process was composed by two etching steps in Ar and Ar/H₂ mixtures, respectively, followed by the deposition in an Ar/C₂H₂ environment. During these steps, the temperature of the rubber varied as a result of ions impingement. Therefore, depending on the bias voltage and treatment time, the temperature variations during deposition (ΔT) can be controlled, and the microstructure of the film (i.e., the patch size) can be tailored due to the different thermal stresses during the growth.⁸ The process time was set in order to obtain a thickness of the DLC film of ~ 300 nm in all the cases. Further details of deposition can be found elsewhere.^{8,9}

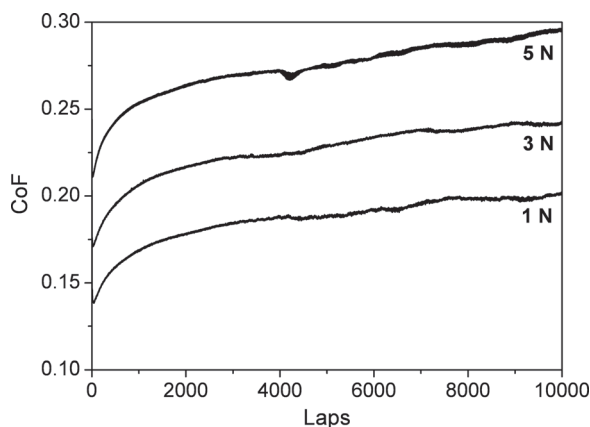


FIG. 2. Frictional curves for a DLC-covered ACM substrate under three different loads.

The microstructure was characterized by scanning electron microscopy (SEM), using a Philips FEG-XL30 operating at 3 kV acceleration voltage. Cross sections of DLC film coated rubber were obtained by fracture after immersion in liquid nitrogen for 10 min. Three-dimensional images were obtained with a Nanofocus confocal microscope and a Digital Instruments Nanoscope IIIa atomic force microscopy operating in tapping mode using a Si tip. The CoFs of the films were evaluated in a CSM ball-on-disk system operating against 6 mm diameter 100Cr6 steel balls in air at a relative humidity of $35\% \pm 2\%$. In some cases, a ball coated with a DLC film was used. The test parameters were set to 10 cm/s of linear speed, test radius between 7 and 13 mm, and at least 10 000 laps of sliding distance. Some tests were performed with oil lubrication, by adding some drops of Shell T9 lubricant on the wear track at the beginning of the tribotest. The oil was not replenished during the tribotest.

III. RESULTS AND DISCUSSION

The overall CoF observed in this system (μ) can be decoupled into adhesive (μ_{Adh}) and hysteresis viscoelastic (μ_{Hyst}) contributions as¹⁶

$$\mu = \mu_{Adh} + \mu_{Hyst}. \quad (1)$$

The adhesive component is mainly related to the adhesion between two surfaces in contact,¹⁶

$$\mu_{Adh} = \frac{A \cdot S}{L}, \quad (2)$$

where A is the contact area, S is the shear strength, and L represents the applied load. Assuming a Hertzian contact and a circular contact area, we can write

$$\mu_{Adh} = \frac{K_1 \cdot L^{2/3} \cdot S}{L} = K_{Adh} L^{-1/3}, \quad (3)$$

where K_1 includes geometrical parameters and substrate properties.

Different approaches can be followed to estimate the viscoelastic contribution to the CoF.¹⁶ In the case where the substrate is considered as a “matress” formed by Voigt units, the following expression is obtained:

$$\mu_{Hyst} = K_{Hyst} \cdot L^{1/2}. \quad (4)$$

Another option is to use a modified elastic model to evaluate the response of the substrate, which yields to the following equation:

$$\mu_{Hyst} = K'_{Hyst} \cdot L^{1/3}. \quad (5)$$

It is worth mentioning that, whatever approaches is followed, the exponent of the load in the viscoelastic contribution to the CoF is positive, while it is negative in the case of the adhesive one. All the constants (K) in Eqs. (3)–(5) do not depend on the applied load, but depend on the materials properties and geometry. Thus, they depend on the lap

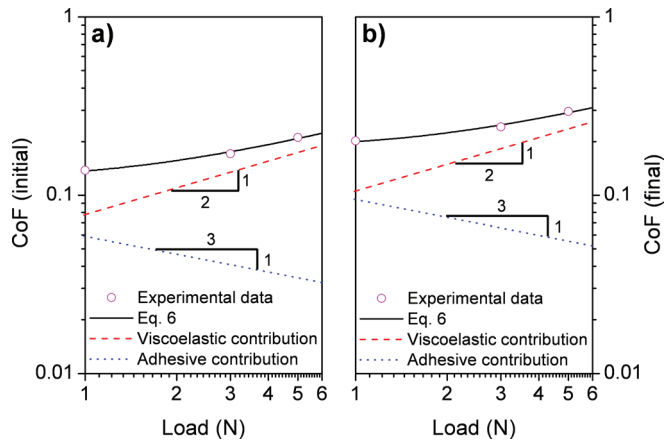


FIG. 3. Fitting of the CoF to the equation (6), at the beginning (a) and at the end (b) of the tribotests presented in Figure 2.

number, since the viscoelasticity of the substrates causes variations in the depth, size, and geometry of the contact area.

In order to discriminate the viscoelastic and adhesive contributions, two different experimental strategies have been applied. The first one consists of using the different dependences on load of both contributions by performing dry tribotests under different loads on two different samples. In the second one, the adhesive strength between the DLC film and the counterpart is modified while keeping the other test parameters constant, which will only influence the adhesive component (cf. Eq. (2)).

Figure 2 shows the CoF evolution of the same sample at three different test loads. It can be seen that the CoF increases during the test for the three loads. In addition, the samples tested at higher loads show higher values of CoF. Figure 3 shows the fitting of the friction coefficient of one sample tested at different loads to the following expression (assuming the “mattress” Voigt approach for the hysteresis contribution, Eq. (4)):

$$\mu = K_{Adh} \cdot L^{-1/3} + K_{Hyst} \cdot L^{1/2}. \quad (6)$$

Two values of the friction coefficient have been monitored for each test, the initial and the final ones. In both situations, the adhesive contribution is much lower than the viscoelastic one, in contrast to what is observed in non-protected rubbers.¹⁶ This is because the DLC film significantly reduces the adhesion between the steel ball and ACM rubber. Besides, it can be seen that the adhesive component has a stronger increase than the viscoelastic one when comparing the initial and final situations. This fact indicates that the

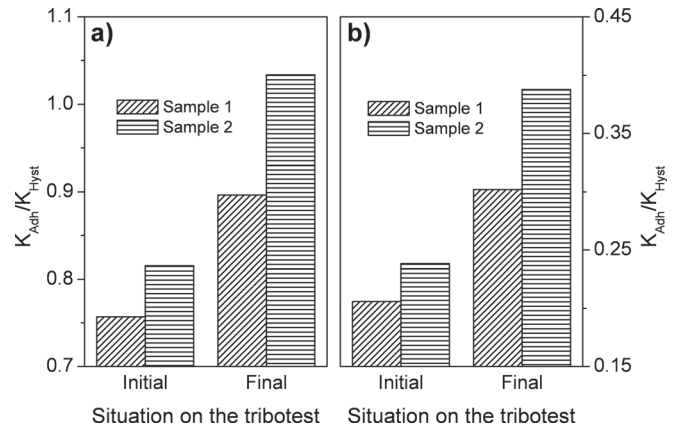


FIG. 4. Evolution of the adhesive-to-viscoelastic ratio from the beginning to the end of the tribotest. (a) After using a “mattress” Voigt approach for the viscoelastic contribution (Eq. (4)). (b) After using a modified elastic approach for the viscoelastic contribution (Eq. (5)).

adhesive contribution would be the main responsible of the overall friction increase during the test.

The values of K_{Adh} and K_{Hyst} can be obtained from the fittings (they correspond to the values of the components of the fitting functions at 1 N load, cf. Eq. (6)). The adhesive-to-viscoelastic ratio (K_{Adh}/K_{Hyst}) is therefore a good parameter for monitoring the changes of CoF. It can be seen in Figure 4 that this ratio increases from the initial to the steady state, for two different samples and both models used for the viscoelastic contribution (cf. Eqs. (4) and (5)). This indicates that the adhesive contribution to friction increases more than the viscoelastic one during the test, which supports the previous observations.

Nevertheless, this method is not so accurate, since the equations used are too simple to account for the mechanisms involved. For instance, regarding the adhesive contribution, the real contact is non-Hertzian, since the deformation is not purely elastic, and the contact area is not circular. Similar simplifications are also used for the viscoelastic contributions.

Therefore, a second strategy has been followed to investigate the nature of CoF. Four tribotests have been performed by varying the shear strength by using two types of balls (uncoated steel and DLC coated steel), during dry and lubricated tests. These tests have been performed at 1 N load and keeping the other parameters constant on three different samples: two specimens coated under different conditions ($\Delta T = 0^\circ\text{C}$ and $\Delta T = -94^\circ\text{C}$) and an uncoated one for comparative purposes. The tests characteristics and average CoFs (in the last 8000 cycles) are summarized in Table I.

TABLE I. Tribotest conditions and CoF of the samples.

Tribotest conditions			CoF of different samples		
Test diameter (mm)	Counterpart material	Oil lubrication	Uncovered ACM	$\Delta T = 0^\circ\text{C}$ (smooth)	$\Delta T = -94^\circ\text{C}$ (rough)
26	Steel	No	0.711 ± 0.133	0.219 ± 0.009	0.198 ± 0.006
18	DLC	No	0.755 ± 0.055	0.108 ± 0.002	0.152 ± 0.004
22	Steel	Shell T9	0.048 ± 0.001	0.091 ± 0.002	0.159 ± 0.001
14	DLC	Shell T9	0.048 ± 0.0003	0.077 ± 0.001	0.133 ± 0.002

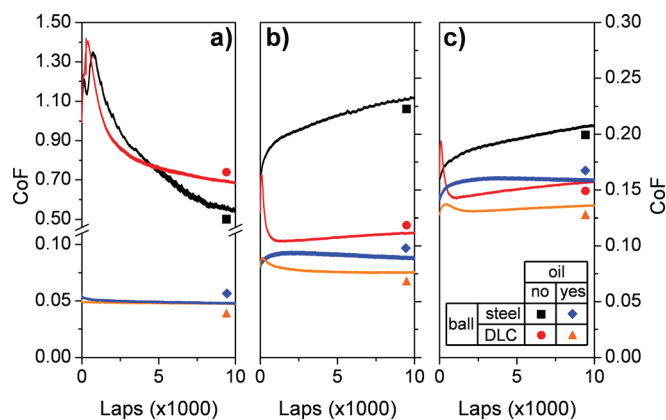


FIG. 5. CoF curves in different sliding conditions (see Table I). (a) Uncoated rubber. (b) Rubber coated with a “smooth” DLC film, deposited at $\Delta T = 0^\circ\text{C}$. (c) Rubber coated with a “rough” DLC film, deposited at $\Delta T = -94^\circ\text{C}$. The *y* axis of (b) is the same that in (c).

Figure 5 plots the results of the tribotests summarized in Table I. A large variation of the results can be observed, which points at an adhesive interaction (see Eq. (2)). The uncoated rubber without oil lubrication shows a very high friction (cf. Figure 5(a)), even in the case of sliding against DLC-coated ball. A very low friction coefficient (ca. 0.048) is seen with oil lubrication in both cases. In fact, in the case of steel ball (blue line), a slight decrease of friction coefficient is seen during the test. This is related to the viscoelastic contribution to the friction coefficient, which is only observed in case of a practical lack of adhesive friction and will be further discussed. Both samples of DLC films coated ACM rubber show similar behaviors (i.e., curve shapes) under equivalent test conditions (cf. Figures 5(b) and 5(c)). The sample prepared at $\Delta T = -94^\circ\text{C}$ is better in the case of dry sliding against steel ball, in agreement with the results reported previously.^{8,10} While dry sliding against a DLC coated ball, the friction coefficient is reduced further, in agreement with an adhesive mechanism. Nevertheless, the CoF keeps growing with increasing number of cycles. Further, in the case of using a DLC coated ball, a running-in period is seen for both non-lubricated and lubricated conditions (red and orange lines). This effect is attributed to a DLC-DLC interaction, and it appears less intense in the presence of oil lubrication. Both tests with oil lubrication (blue and orange lines) show lower values for the sample prepared at $\Delta T = 0^\circ\text{C}$, but still higher than the values observed for the uncoated rubber. This can be explained by the different nature of the surface of the different samples.

Figure 6 shows cross section SEM images of the DLC-protected rubbers. It can be seen that they present a very different structure, as a consequence of the different temperature variation during the film growth.^{8,9} The DLC film deposited at $\Delta T = 0^\circ\text{C}$ is more flat, in contrast to the curved patches of the DLC film grown at $\Delta T = -96^\circ\text{C}$. The depth of these “valleys” has been estimated by means of AFM and confocal microscopy. Figure 7(a) depicts the top view of the sample under study, indicating the regions measured by confocal microscopy and AFM with squares (see Figures 7(b) and 7(c)). The silver patches indicated in the image were

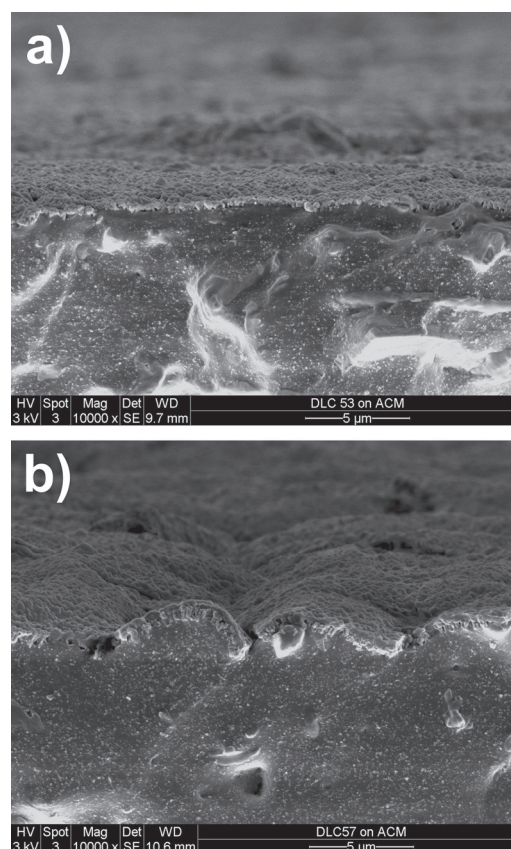


FIG. 6. Cross section SEM images of the DLC coated rubbers. (a) $\Delta T = 0^\circ\text{C}$ and (b) $\Delta T = -94^\circ\text{C}$.

used as markers to locate the same region of the sample. The green line represents the region where the profiles plotted in Figure 7(d) were taken. It can be seen that the AFM cannot reach the bottom of the valley due to the limited vertical displacement of the scanning cantilever probe. The confocal microscopy could reach the bottom of the valley, but only up to certain points. This is because of the low reflectivity of the sample, which is even reduced in the case of high slopes (i.e., the sides of the valley). By combining the data from both techniques, a valley depth of ~ 4 to $\sim 5.5 \mu\text{m}$ can be estimated in the profiles depicted in Figure 7(d), confirming the high “roughness” of this sample.

Therefore, the different behavior of the samples under oil lubrication can be explained as the following (see sketches in Figure 8). The uncoated ACM rubber appears relatively smooth and can be covered effectively by an oil layer (Figure 8(a)). In the case of DLC film deposited at $\Delta T = -94^\circ\text{C}$, as demonstrated previously, the film surface is formed by curved patches, and the oil cannot fully separate the DLC film from the counterpart (Figure 8(c)). Finally, the sample prepared at $\Delta T = 0^\circ\text{C}$ represents an intermediate situation (Figure 8(b)). This interpretation is confirmed by comparing both tests performed with lubrication on the three samples (cf. Figure 5). In the case of the uncoated ACM, no difference of CoF is observed between steel ball or DLC coated steel ball, indicating a good isolation of rubber surface from the counterpart by the oil layer. In contrast, when the rubber is protected with a DLC film,

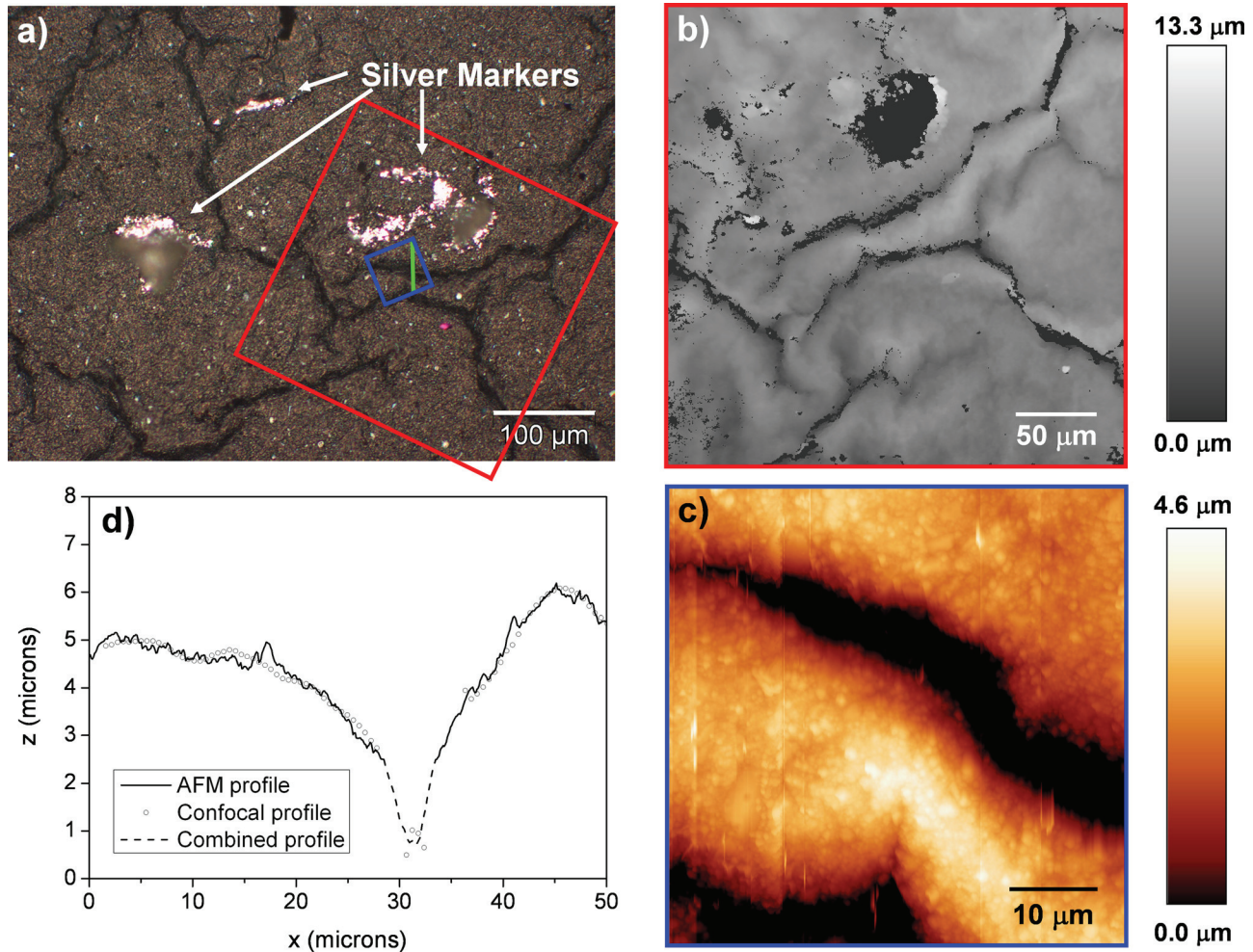


FIG. 7. Characterization of a crack in the sample prepared at $\Delta T = -94^\circ\text{C}$. (a) SEM image; (b) confocal image; (c) AFM image; and (d) crack profile. The squares in the SEM image represent the confocal and the AFM images, and the green line represents the place where the profiles were taken.

the friction is lower while sliding against the DLC coated ball as compared to sliding against the steel ball, indicating a certain interaction with the counterpart. In fact, the reduction is greater for the “rough” film, confirming a greater interaction in that case.

The behavior of the different samples against steel ball in the presence of oil is of particular interest, since it represents a situation where the adhesive contribution to friction

is minimized. Figure 9 shows the CoF behavior for extended tribotests up to 30 000 laps. In all cases, the CoF shows a decreasing behavior with increased number of laps. This behavior agrees with the expected variation of the viscoelastic contribution with the number of laps, according to the theoretical predictions.¹³

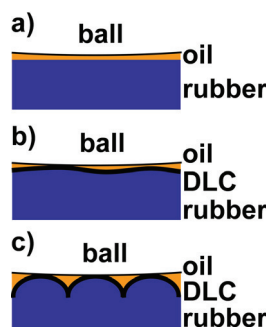


FIG. 8. Scheme of the oil distribution for three different situations. (a) Uncoated rubber. (b) Rubber coated with a “flat” DLC film, deposited at $\Delta T = 0^\circ\text{C}$. (c) Rubber coated with a “rough” DLC film, deposited at $\Delta T = -94^\circ\text{C}$.

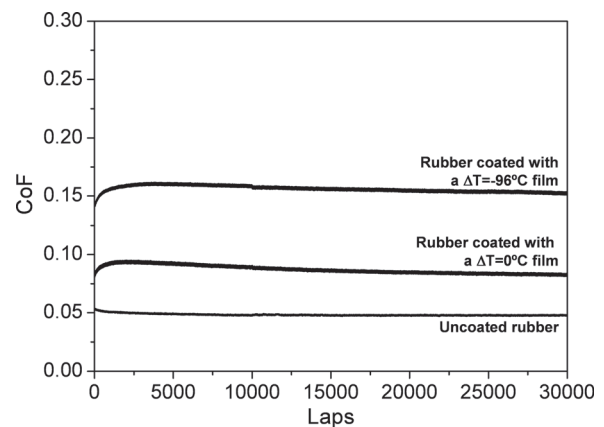


FIG. 9. Extended frictional curves of the different samples against steel counterpart under oil lubrication.

IV. CONCLUSIONS

Two different experiments have been designed to reveal the nature of the CoF of DLC film-protected rubbers, by modification of the loads and shear strength between the surfaces in contact. Under non-lubricated conditions, the increase of CoF during the tribotests is caused by an increased adhesive interaction. This is the consequence of the substrate viscoelasticity, which leads to larger contact areas at higher number of laps. The viscoelastic contribution is of secondary importance, and it is only observed when the adhesive one is minimal. It decreases with the number of laps, in agreement with the predicted variation of the shape of the contact area. Finally, a low surface roughness has been identified as a critical parameter for a more efficient liquid lubrication.

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